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## PATENT SPECIFICATION

1,112,617

NO DRAWINGS.

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Date of filing Complete Specification: 23 Dec., 1966.

Application Date: 23 Nov., 1965. No. 49698/65.

Complete Specification Published: 8 May, 1968.

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Index at Acceptance:—C1 A(D10, G50) AG50D10.

Int. Cl.:—C 01 d 3/08.

## COMPLETE SPECIFICATION.

## Recovery of Sodium Chloride in the Production of Bleached Pulp.

We, ELECTRIC REDUCTION COMPANY OF CANADA LTD., a Canadian company of 155 Etobicoke Drive, Toronto (Islington) Ontario, Canada, formerly of 137 Wellington Street, West, Toronto, Ontario, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the removal of sodium chloride from the furnace fume produced during the recovery of chemicals used in the pulping of cellulosic fibrous materials.

In the conventional Kraft process for the production of bleached cellulosic fibrous pulp, or modifications thereof such as the Alkalide process, the cellulosic fibrous material is heated in a digestion stage with a "white liquor" which contains sodium sulphide and which may also contain sodium hydroxide to dissolve the hemicelluloses, lignin and other extractable or organic materials contained in the fibrous material. The digested fibrous pulp so obtained is separated from the resultant "black liquor", the latter being sent to a recovery stage and the former being sent to a bleaching stage. The above process is of especial application to the pulping of wood chips.

In the recovery stage, the black liquor is concentration by evaporation of water therefrom and the concentrated liquor then burnt in a furnace to yield a smelt containing sodium carbonate and sodium sulphide. The smelt is quenched with water to form a raw green liquor which is then clarified. The clarified green liquor is causticized with the lime to convert the sodium carbonate present in the liquor to sodium hydroxide. The calcium carbonate which is precipitated during the causticization of the liquor is sepa-

rated therefrom as a mud and calcined to regenerate lime for further causticization. The filtered causticized green liquor is the white liquor which is used in the digestion stage and is recycled to treat further fibrous material. Sodium sulphate is usually added to the evaporation and furnacing steps of the recovery stage of the process to make up any loss of chemicals in these stages. In the above process, it is found that sodium chloride builds up to a steady state concentration in the white liquor and throughout the recovery system. Sodium chloride represents a "dead load" which must be carried by the system since it is inactive in the whole pulping and recovery process. This requires larger equipment throughout the process and a higher recycle rate than would otherwise be necessary.

One major source of the sodium chloride is the wood chips used in the digestion stage. Frequently the logs from which the wood chips are prepared have been floating in sea water and have therefore absorbed large quantities of salt. This salt is introduced directly into the pulping process via the wood chips. Attempts have been made to reduce the amount of sodium chloride in the wood chips prepared from sea water soaked logs by washing the logs with fresh water, but this entails further handling of the logs which is expensive and, although the quantity of sodium chloride is reduced, it is not completely eliminated. In fact, the pulping industry generally accepts the introduction of from 10 to 20 lbs. of salt into the liquors in the pulping process per ton of pulp produced.

Furthermore, where a pulping process is used in which the effluent from the caustic extraction step, following the first bleaching step in the bleaching stage of the process, is used to dissolve the smelt, (as described and

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claimed in our copending Application No. 3130/65 (Serial No. 1,106,841) further sodium chloride is introduced into the liquors of the digestion and recovery stages. This is so since the sodium hydroxide used in the caustic extraction step reacts with any unreacted chlorine retained in the pulp from the bleaching stage to form sodium chloride which is retained in the effluent from the caustic extraction stage which is then used in the digestion and recovery steps.

It will be readily realized that the sodium chloride build-up in the liquors of the recovery and digestion stages of the pulping process presents a problem and the attempts made hitherto to reduce or eliminate the sodium chloride from the liquors have not been commercially successful.

Although it is known that the deposit obtained in the flue of the furnace in which the black liquor is burnt to produce the smelt contains a substantial proportion of the sodium chloride in the burnt chemicals, in admixture with sodium sulphate, sodium carbonate and other minor constituents, it has been considered that the removal of sodium chloride from the system by discarding the fume deposit from the process is uneconomical due to the coincidental loss of relatively large amounts of sodium sulphate. It has therefore been the practice to return the fume deposit containing the sodium chloride to the recovery stage of the process since no satisfactory method for removing the sodium chloride only from the fume has yet been devised. We now find that, if the fume deposit is subjected to extraction with water, much of the sodium chloride, being dissolved preferentially, may be removed in an economical manner from the system. Moreover, the solids remaining are enriched in sodium sulphate which may then be returned to the pulping process thus maintaining the economics of recycling the fume without the attendant disadvantage of recycling large amounts of sodium chloride.

Accordingly, the present invention provides in a process for the pulping of cellulosic materials wherein the cellulosic material is digested in known manner in an aqueous solution containing sodium hydroxide and/or sodium sulphide, and the spent digestion liquor is sent to a recovery system wherein it is burnt in a furnace to produce a smelt which is dissolved in water, clarified and causticized in known manner, and a fume containing sodium chloride and sodium sulphate, the improvement which comprises leaching the fume with water to produce a solution rich in sodium chloride.

In carrying out the process of the invention a pulping process is performed in the normal manner and the spent black liquor burnt in the customary manner. The fume

may be recovered from the furnace off-gases during burning using conventional equipment, for example electrostatic precipitators. The fume contains, *inter alia*, sodium chloride, sodium sulphate and sodium carbonate in proportions which vary over a broad range and are dependant upon a variety of conditions. Whilst the process of the invention is applicable to the treatment of fumes containing any proportions of sodium chloride, it is of especial application in the treatment of fumes containing a major proportion of sodium sulphate, for example fumes containing sodium chloride and sodium sulphate in molar proportions of 1:3 and more, which are obtained from a typical coastal mill.

The leaching of the fume may be carried out using conventional leaching techniques. The amount of water employed to leach out the sodium chloride is preferably no more than that theoretically required to produce a solution saturated with sodium chloride though a slight excess, to allow for the solution of sodium sulphate which concurrently occurs, is preferred. The use of these amounts of water usually results in the formation of a slurry of the fume in water containing, for example about 200%, solids content. The slurrying may be carried out at ambient temperatures, though the use of hot water is of advantage. In order to aid the preferential solution of the sodium chloride from the fume it is preferred to use aqueous solutions which are already saturated with respect to sodium sulphate to leach the fume.

The products of the leaching process of the invention are an aqueous solution containing a higher proportion of sodium chloride than the fume and undissolved solids which contain the major proportion of the sodium sulphate present in the fume. For example, where a fume containing sodium chloride and sodium sulphate in a molar proportion of about 1:3 is leached with hot water, the leach liquors contain the salts in a molar ratio of about 9:1. The leach liquors may then be separated from the undissolved solids in known manner, such as filtration or centrifuging.

The process of the invention removes a substantial proportion of the sodium chloride present in the furnace fume and thus permits recycling of the leached fume to the pulping process without appreciably increasing the chloride load of the pulping chemicals. Alternatively, the leached fume may find use elsewhere in a paper making process. For example, instead of recycling the leached fume to the furnace, it may be employed to provide sulphuric acid and/or sodium hydroxide which find use elsewhere in the paper making process.

The leach liquors containing the major

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- proportion of the sodium chloride originally present in the fume may be discarded, thus eliminating the chloride from the pulping system. However, this discard represents a loss of chemicals from the system and in some cases it may prove desirable to recover the chemicals for use elsewhere. In particular the leach liquors find use as a source of sodium chloride in production of chlorine and chlorine dioxide by the reaction of sodium chloride, sodium chlorate and sulphuric acid. Whilst it is possible to use the slurry of undissolved solids in leach liquor obtained by the leaching of the fume, such a slurry contains a large amount of undissolved material which represents a dead weight which must be cycled through the chlorine/chlorine dioxide generator. It is therefore preferred to use the leach liquors alone as the source of the sodium chloride since the sodium sulphate present in the leach liquors is in solution and does not present as great a dead weight as the undissolved solids. A particularly suitable chloride dioxide generator in which the leach liquors could be used is that described and claimed in our copending Application Nos. 50770/64, 33092/64, 33093/64, (Serial Nos. 1,057,017, 1,056,790, 1,077,306. Such a use of the leach liquors with or without the solids, in effect removes the sodium chloride from the sodium sulphate which may be recovered in the substantially pure form from the generator effluent.
- WHAT WE CLAIM IS:—
1. In a process for the pulping of cellulosic materials wherein the cellulosic material is digested in known manner with an aqueous solution containing sodium hydroxide and/or sodium sulphide, and the spent digestion liquor is sent to a recovery system wherein it is burnt in a furnace to produce a smelt, which is dissolved in water, clarified and causticized in known manner, and a fume containing sodium chloride and sodium sulphate, the improvement which comprises leaching the fume with water to produce a solution rich in sodium chloride.
  2. A process according to claim 1 wherein the fume contains sodium chloride and sodium sulphate in a molar ratio of about 1:3.
  3. A process according to either of claims 1 or 2 wherein a slurry of the fume in water is formed.
  4. A process according to any of the preceding claims wherein the solution rich in sodium chloride is separated from the undissolved solids.
  5. A process according to any of the preceding claims wherein the slurry or the aqueous solution rich in sodium chloride is used to supply at least part of the sodium chloride required for the generation of a mixture of chlorine and chlorine dioxide by the reaction of sodium chloride, sodium chlorate and sulphuric acid, which mixture is then used to bleach the digested cellulosic material.
  6. A process according to claim 4 wherein the undissolved solids are recycled to the furnace.
  7. A process according to claim 4 wherein the undissolved solids are treated to liberate sulphuric acid and sodium hydroxide therefrom.
  8. A process according to any of the preceding claims wherein the cellulosic material is wood.
  9. Cellulosic fibrous materials whenever bleached by a process as claimed in claim 5.
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